Estimation of highest burning rate of AP/HTPB composite propellant with experimental approach (II)

- Estimation of highest burning rate by use of AP particle property -

Makoto Kohga and Yutaka Hagihara

The upper limit content of AP incorporated in AP/HTPB composite propellant, ϕ_{max} exists because of the requirements for the preparation of propellant. The burning rate increases with increasing the AP content and the burning rate of the propellant prepared at ϕ_{max} , r_{ϕ} is the highest value of the propellant prepared with AP used as an oxidizer. It is necessary to estimate r_{ϕ} because the burning rate is one of the important properties for the propellant design. An attempt was made to find out the estimation of r_{ϕ} with the experimental approach in this study.

As the specific surface area, S_W increases, r_o increases below 700 m²·kg⁻¹ and decreases above that. This relationship is expressed by a convex line. It is found that the r_{ϕ} can be estimated by S_{W} on the basis of the plot of r_o versus S_w . The upper limit of r_o exists and r_o of propellant prepared with AP, of which S_w is 700 $m^2 \cdot kg^{-1}$, is the maximum value of AP/HTPB composite propellant. The maximum of r_o is 25.2 mm·s⁻¹ at 7 MPa in this study. It is found that r_{ϕ} is dependent on ϕ_{max} and S_{W} greatly, and the maximum value of r_{ϕ} could be obtained at the particular combination of ϕ_{max} and S_W . The effect of ϕ_{max} on r_ϕ was corrected by the multiplication of ϕ_{max} by the increasing ratio of the burning rate upon S_w . The effect of S_w on r_o was corrected by the multiplication of S_W by the increasing ratio of the burning rate upon the AP content.

1. Introduction

For the design of a composite propellant, the burning rate is one of the important properties. As the burning rate increases, the amount of combustion gas per unit time increases and larger thrust could be obtained. Therefore, a higher burning rate propellant is required. The burning rate of ammonium perchlorate (AP)/ hydroxyl - terminated polybutadiene (HTPB) composite propellant increases with increasing AP content. The larger AP content of the propellant should be required to obtain the higher burning rate AP/HTPB composite propellant. The upper limit content of AP incorporated in propellant, ϕ_{max} exists because of the requirements for the preparation of AP/HTPB composite propellant^{1, 2)}. The burning rate of the propellant prepared at ϕ_{max} , r_{ϕ}

Received: May 19, 2003

Department of Applied Chemistry, National Defense Academy, 1-10-20, Hashirimizu, Yokosuka-shi, Kanagawa, 239-8989, Japan

TEL +81-46-841-3810 (ext. 3585)

FAX +81-46-844-5901 E-Mail kohga@nda.ac.jp

Accepted: June 10, 2003

order to develop the estimation of r_o with the experimental approach. The following results were obtained: 1) The ranges of ϕ_{max} and r_{ϕ} at 7 MPa are 72 -85 wt% AP and 11.7 - 25.2 mm·s⁻¹, respectively. 2) The increment of burning rate increased remarkably with coming close to ϕ_{max} . The increasing ratio of the burning rate upon the AP content, α increases with increasing specific surface area less than 500 m²·kg⁻¹,

is the highest value of the propellants prepared with AP

used as an oxidizer. It is important for the design of

AP/HTPB composite propellant to estimate r_o . The

burning rate characteristics of AP/HTPB composite

propellant have been investigating, however, ro have

In the previous study³⁾, a lot of propellants were

prepared with many kinds of AP samples, e.g. spherical

AP, porous AP, hollow AP, narrow distribution, wide

distribution, monomodal, bimodal, etc., and the burning

rate characteristics of the propellants were investigated in

little been published to date.

and is the maximum and almost constant above that. 3) The increasing ratio of the burning rate upon the specific surface area, β increases linearly with the AP content. In this study, an attempt was made to find out the estimation of r_{ϕ} on the basis of the previous paper³⁾.

2. Experimental

The particle properties of AP samples are shown in Table 1. These samples were the same as materials used in the previous report³⁾. Samples A-E were prepared by grinding commercial AP for 5, 10, 20, 30 and 40 minutes in a vibration ball mill. The shape of samples A -E was spherical and the particle size distribution was wide. Sample F was prepared by shifting sample E. Sonic sifter was used as a sifter. Sample F was AP particles passed $38 \,\mu$ m. The shape of sample F was spherical and this particle size distribution was narrow.

Samples G-Q were prepared by the spray-drying method⁴⁻⁶⁾. Samples R and S were prepared by the freeze-drying method⁷⁾. The shapes of samples G-I, samples J-O and samples P-S were spherical, porous and hollow, respectively. Samples a-h were the mixture of two AP samples and, therefore, these distributions were bimodal. The mean volume-surface diameter on number basis, D_{vx} and the specific surface area, S_{W} are shown in Table 1. The D_{vx} was measured by use of the SEM photographs and S_{W} was determined by air-permeability method. The ranges of D_{vx} and S_{W} are 2-110 μ m and 40-1200 m²·kg⁻¹, respectively.

The burning rate characteristics were also investigated in the previous report. Table 1 also shows ϕ_{max} , r_o , and α . Table 2 shows the value of β at each AP content.

Table 1 Particle properties of AP and burning rate characteristics of propellant

Symbol	D., (μm)	S-(m²·kg-1)	φ _{max} (wt%)	$r_{\phi} (\text{mm} \cdot \text{s}^{-1})$		α (-)	0 ()
				1 MPa	7 MPa	α (-)	β _φ (-)
A	110	40	85	5. 3	11.7	1.7	0.0400
В	70	50	85	5. 3	12.1	1.9	0.0400
С	50	100	84	5.4	12.4	2.1	0.0376
D	40	150	83	5. 4	12.8	2.6	0.0364
E	40	180	83	5. 5	14. 2	3. 1	0.0364
F	20	260	82	5.7	15. 1	3.5	0.0334
G	2	1010	75	6. 2	16.9	4.6	0.0113
Н	2	940	76	6. 9	19.8	4.7	0.0163
I	3	900	77	7. 2	21.8	4.3	0.0182
J	6	1060	73	5.8	15.4	5. 2	0.0061
K	8	450	80	6. 9	19. [4.5	0.0298
L	7	780	77	7.4	24. 2	5.5	0.0182
M	4	840	77	7.1	23. 1	4.5	0.0182
N	3	990	74	6. 2	17.2	5.1	0.0094
0	4	860	76	7.1	21.1	4.8	0.0163
P	3	1200	72	4.7	13.1	5.0	0.0046
Q	3	1160	72	5. 2	12.2	4.7	0.0046
R	4	610	80	9.3	24.6	4.9	0.0274
S	11	370	81	7. 5	19.5	5. 2	0.0298
a	2	480	80	7. 2	20.5	4.7	0.0274
b	10	470	80	7. 3	19.8	4.9	0.0274
С	5	550	80	8. 9	22.8	4.5	0.0274
d	9	220	83	5. 9	13.5	3.0	0.0364
e	6	310	82	6. 2	14. 2	3. 5	0.0334
f	2	820	78	7. 2	22. 2	5. 2	0.0215
g	2	690	79	8. 9	25. 2	5. 1	0.0240
h	2	630	79	9. 1	25. 1	5.4	0.0240

Table 2	Value of	B	at each AP	content
---------	----------	---	------------	---------

AP content (wt%)	β (-)		
72	0.0046		
73	0.0061		
74	0.0094		
75	0.0113		
76	0.0163		
77	0.0182		
78	0.0215		
79	0.0240		
80	0. 0274		
81	0.0298		
82	0.0334		
83	0.0364		
84	0.0376		
85	0.0400		

3. Results and discussion

3. 1 Estimation of r_{ϕ}

The burning rate is affected by the AP content. This suggests that r_{ϕ} would be related to ϕ_{max} . Figure 1 shows the dependence of ϕ_{max} on r_{ϕ} . As ϕ_{max} increases, r_{ϕ} increases less than 79.5 wt% AP and decreases above that. The r_{ϕ} is greatly influenced by the AP content, however, the values of r_{ϕ} are different at constant ϕ_{max} . For example, the values of ϕ_{max} for propellants K, R, b and c are constant, 80 wt% AP, and r_{ϕ} of these propellants is different from one another according to Table 1. The difference in r_{ϕ} between

propellants K and R is 5.5 mm s⁻¹ at 7 MPa and this value cannot be neglected with regard to estimation of r_{ϕ} . These results indicate that r_{ϕ} is influenced by ϕ_{max} , however, r_{ϕ} cannot be estimated by ϕ_{max} only.

The burning rate increases with decreasing diameter of AP or increasing specific surface area. The flame of AP composite propellant is a so called diffusion flame, and the model of Multiple Flames⁸⁾ is generally accepted as a model of the flame structure. According to the model of Multiple Flames, the oxidizer and binder decomposition products diffuse and mix and, consequently, the combustion occurs. It can be considered that the combustion of AP occurred on the surface of AP particle. Some porous and hollow AP samples were used in this study. This suggested that S_W would be an appropriate property to express the surface area of AP particle contributes to the combustion, compared with D_{ij} . The S_W was used as the particle property to represent the size of AP particle relates to combustion in the following discussion.

The ϕ_{max} of propellant A is the largest in this study, however, r_{ϕ} of this propellant is the lowest. This would be because S_{W} of sample A is small. It can be considered that r_{ϕ} would be greatly dependent on ϕ_{max} and S_{W} and the highest value of r_{ϕ} could be obtained at the particular combination of ϕ_{max} and S_{W} . The ϕ_{max} can be estimated with S_{W}^{2} . These suggests that r_{ϕ} can be expressed by S_{W} . Figure 2 shows the dependence of S_{W} on r_{ϕ} . As S_{W} increases, r_{ϕ} increases below 700 m²·kg⁻¹ and decreases above that. The relationship is expressed by a convex line. It is found that r_{ϕ} can be estimated

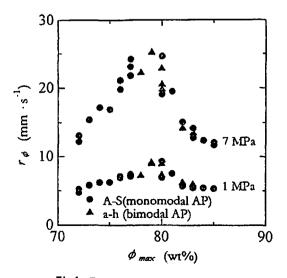


Fig.1 Dependence of ϕ_{max} on r_o

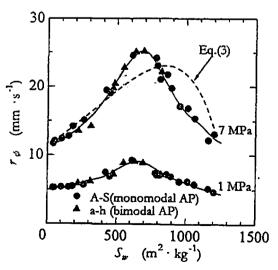


Fig.2 Dependence of Sw on ro

estimated by S_W on the basis of Fig.2.

The plot of log (burning rate) against log (pressure) for the propellant prepared at ϕ_{max} is approximately linear³⁾. The r_o at certain pressure could be estimated almost exactly by the straight line drawing with two points, the values of r_o at 1 MPa and 7 MPa, on a log (burning rate) – log (pressure) graph. The r_o at 1 MPa and 7 MPa can be estimated by S_W on the basis of Fig.2.

If the preparation of the propellant was different from that in this study, the value of r_o would be varied. However, it was expected that r_o could be estimated by S_w .

3. 2 Quantitative analysis

The relationship between r_{ϕ} and S_{W} is represented by a convex line as shown in Fig.2. This suggested that r_{ϕ} would be affected by two factors that one factor would cause to increase r_{ϕ} and another factor would cause to decrease r_{ϕ} as S_{W} increases. The influences of these two factors on r_{ϕ} were analyzed quantitatively below on the basis of the burning rate characteristics.

As mentioned in the previous section, r_o would be influenced by ϕ_{max} and S_W greatly. The α represents the increasing ratio of the burning rate upon the AP content at the constant S_W . As S_W increases, α increases less than $500 \text{ m}^2 \cdot \text{kg}^{-1}$ and is approximately constant and the maximum above that³⁾. It could be considered that the influence of S_W on r_o could be expressed by the product of α and S_W . The αS_W was calculated on the basis of the data as shown in Table 1. Figure 3 shows the influence of S_W on αS_W . The αS_W increases with increasing S_W . It seems that the relationship is linear. However, the relationship is

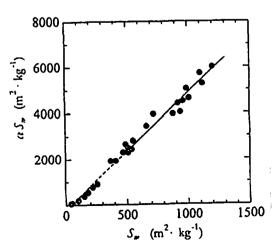


Fig.3 Influence of Sw on αSw Relationship

represented by a parabola line less than approximately $500 \text{ m}^2 \cdot \text{kg}^{-1}$, the broken line, in the case of the magnified scale because α increases with increasing S_W less than $500 \text{ m}^2 \cdot \text{kg}^{-1}$.

The β represents the increasing ratio of the burning rate upon S_W at the constant AP content. The β increases linearly with the AP content. The β corresponding to ϕ_{max} , β_{ϕ} of each AP sample was determined on the basis of data as shown in Table 2. The results are also shown in Table 1. It could be considered that the influence of ϕ_{max} on r_{ϕ} could be expressed by the product of β_{ϕ} and ϕ_{max} . The β_{ϕ} ϕ_{max} was calculated on the basis of the data as shown in Table 1. Figure 4 shows the influence of S_W on β_{ϕ} ϕ_{max} . The β_{ϕ} ϕ_{max} decreases linearly with increasing S_W .

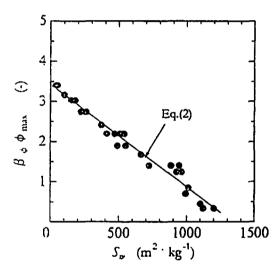


Fig.4 Influence of S_{W} on $\beta_{\phi} \phi_{max}$

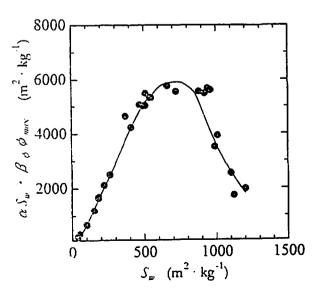


Fig.5 Relationship between $\alpha S_w \cdot \beta_o \phi_{max}$ and S_w

Figure 5 shows the relationship between $\alpha S_W \cdot \beta_{\phi} \phi_{max}$ and S_W . The relationship is expressed by a convex line. The $\alpha S_W \cdot \beta_{\phi} \phi_{max}$ increases below 700 m²·kg⁻¹ and decreases above that, as S_W increases. This convex line is in a similar manner as the relationship between r_{ϕ} and S_W as shown in Fig.2. This fact suggests that r_{ϕ} is dependent on αS_W and $\beta_{\phi} \phi_{max}$ greatly.

The values of both αS_W and $\beta_{\phi} \phi_{max}$ should be larger in order to obtain higher r_{ϕ} . The larger αS_W is, the smaller $\beta_{\phi} \phi_{max}$ becomes as shown in Figs.3 and 4. This indicates that the upper limit of r_{ϕ} exists and r_{ϕ} of propellant prepared with AP, of which S_W is 700 m²·kg⁻¹, is the maximum value according to Figs.2 and 5. The maximum burning rate of AP/HTPB composite propellant is 25.2 mm·s⁻¹ at 7 MPa within the limits of this study.

An attempt was made to obtain the experimental equation to estimate r_{ϕ} at 7 MPa. The ratio of r_{ϕ} to $\beta_{\phi}\phi_{max}$, that is, $r_{\phi}/(\beta_{\phi}\phi_{max})$, was calculated on the basis of Table 1. Figure 6 shows the relationship between $r_{\phi}/(\beta_{\phi}\phi_{max})$ and S_{W} . The $r_{\phi}/(\beta_{\phi}\phi_{max})$ increases with increasing S_{W} . This relationship can be made the approximation with the following equation.

$$r_o/(\beta_o \phi_{max}) = 3.24 \exp(0.002S_W)$$
 (1)

As shown in Fig.4, $\beta_o \phi_{max}$ is closely associated with S_W . The relationship between $\beta_o \phi_{max}$ and S_W can be expressed by the following equation.

$$\beta_o \phi_{max} = 0.0026 S_W + 3.51$$
 (2)

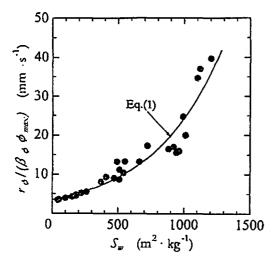


Fig.6 Relationship between $r_o/(\beta_o \phi_{mex})$ and S_W

Substituting Eq. (2) into Eq. (1),

$$r_o = (0.0026S_W + 3.51) \times 3.24 \exp(0.002S_W)$$
 (3)

Equation (3) is expressed by the broken line in Fig.2. Equation (3) is a convex line, however, this equation could not agree with the experimental values.

Some porous or hollow AP samples were used in this study. There is the bubble contamination in propellant prepared with porous or hollow AP which influence r_{ϕ} . In addition, r_{ϕ} would be not only affected by ϕ_{max} and S_W but also by the shape of AP, the distance between two adjacent AP particles in the propellant, the temperature gradient in the vicinity of the burning surface, the diffusion distance and gas reaction in the gas phase, etc. It is necessary to investigate the influences of these factors on the burning rate in order to obtain the accurate experimental equation for the estimation of r_{ϕ} . The experimental equation to estimate r_{ϕ} could not be obtained in this study, however, it is found that r_{ϕ} can be estimated by S_W on the basis of Fig.2.

4. Conclusions

The upper limit content of AP incorporated in AP /HTPB composite propellant exists, ϕ_{max} exists because of the requirements for the preparation of propellant. The burning rate increases with increasing the AP content and the burning rate of the propellant prepared at ϕ_{max} , r_{ϕ} is the highest value of the propellant prepared with AP used as an oxidizer. An attempt was made to find out the estimation of r_{ϕ} with the experimental approach in this study.

As the specific surface area, S_W increases, r_ϕ increases below 700 m²·kg⁻¹ and decreases above that. This relationship is expressed by a convex line. It is found that the r_ϕ can be estimated by S_W on the basis of the plot of r_ϕ versus S_W . The upper limit of r_ϕ exists and r_ϕ of propellant prepared with AP, of which S_W is 700 m²·kg⁻¹, is the maximum value of AP/HTPB composite propellant. The maximum of r_ϕ is 25.2 mm·s⁻¹ at 7 MPa in this study. It is found that r_ϕ is dependent on ϕ_{max} and S_W greatly, and the maximum value of r_ϕ could be obtained at the particular combination of ϕ_{max} and S_W . The effect of ϕ_{max} on r_ϕ was corrected by the multiplication of ϕ_{max} by the increasing ratio of the burning rate upon S_W . The effect of S_W on r_ϕ was corrected by the

multiplication of S_W by the increasing ratio of the burning rate upon the AP content.

The experimental equation to estimate r_{ϕ} could not be obtained because the influences of the other factors, except ϕ_{max} and S_W , on r_{ϕ} could not be revealed within the limits of this experiment. These influences should be investigated in detail for the future in order to obtain the accurate experimental equation to estimate r_{ϕ} .

References

- M. Kohga and Y. Hagihara; Experimental Study on Estimation of Upper Limit of Ammonium Perchlorate Content in Ammonium Perchlorate / Hydroxyl - terminated Polybutadiene Composite Propellant, Trans. Japan Soc. Aero. Space Sci., 41 (132), 74-78 (1998).
- idem;" Estimation of Upper Limit of AP Content in AP/HTPB Composite Propellant —A Consideration Based on Flow Characteristics of AP/HTPB ", J. Ind. Expl. Soc., Japan, 61 (4), 157-166 (2000).
- 3) idem;" Estimation of Highest Burning Rate of AP/

- HTPB Composite Propellant with Experimental Approach (I) Burning Rate Characteristics of AP /HTPB Composite Propellant —", Sci. and Tech. Energetic Materials, Japan, in press
- 4) idem;" The Preparation of Fine Porous Ammonium Perchlorate by the Spray-drying Method", J. Soc. Powder Technol., Japan, 33 (4), 273-278 (1996).
- 5) idem;" The Preparation of Fine Porous Ammonium Perchlorate by the Spray-drying Method The Effect of Organic Solvents on the Particle Shape and Size -", ibid., 34 (6), 437-442 (1997).
- 6) idem;" The Spray-drying of Ammonium Perchlorate by Ultrasonic Commination", ibid., 34(7), 522-527 (1997).
- idem; Preparation of Fine Ammonium Perchlorate by Freeze-Drying, Kagaku Kougaku Ronbunshu, 23 (2), 163-169 (1997).
- 8) M. W. Beckstead, R. L. Derr and C. F. Price;" A Model of Composite Solid- Propellant Combustion Based on Multiple Flames", AIAAJ., 8(12), 2200-2207 (1970).

実験的手法による AP/HTPB 系コンポジット推進薬の 最高燃焼速度の推算(II)

-AP の粒子特性による最高燃焼速度の推算-

甲賀 誠, 萩原 豊

AP/HTPB 系コンポジット推進薬には製造上の条件があるために、推進薬中に混入可能な AP 含有率の上限、 ϕ_{max} がある。AP 含有率の増加にしたがい燃焼速度は増加し、 ϕ_{max} で製造された推進薬の燃焼速度、 r_o が、用いた AP で達成できる燃焼速度の最大値となる。AP/HTPB コンポジット推進薬を設計する上で、 r_o を推測することは重要である。本実験では、実験的手法によって、 r_o を推算する方法を見いだすことを試みた。

用いた AP の比表面積、 S_W が 700 mi-kg^- 以下において、 r_o は S_W の増加にしたがい大きくなり、それ以上では減少した。 r_o と S_W の関係は凸曲線で表された。AP の S_W を測定すれば、その AP の r_o は r_o と S_W の関係をプロットした図から推測できることがわかった。 r_o には上限があり、 S_W が 700 mi-kg^+ となる AP を用いて製造された推進薬の r_o が、AP/HTPB 系コンポジット推進薬が達成できる燃焼速度の最大値となることがわかった。本実験の範囲内では、 r_o の最大値は 25.2 mm·s^+ (7 MPa)であった。 r_o は ϕ_{max} と S_W に大きく依存することがわかった。 r_o に及ぼす ϕ_{max} の影響は、 S_W に対する燃焼速度の増加率を乗ずることによって補正されることがわかった。

("防衞大学校 応用化学科 〒239-8989 横須賀市走水1-10-20)